

Calcium Oxide

Crops

Executive Summary

Calcium oxide was petitioned for use as a soil amendment to supply calcium for crops. Calcium oxide is produced by burning various forms of calcium carbonate such as limestone, marble, chalk, oyster shells, and dolomite. It may also be produced as a by-product of industrial processes such as cement production.

The NOSB refined the definition of synthetic in 1995 and considered the combustion of minerals synthetic. Although the NOSB approved use of calcium hydroxide as a component of Bordeaux mix and lime sulfur for fungicide use, it did not approve use as a soil amendment.

Reviewers all agreed that calcium oxide is a synthetic material. Two of the reviewers support continued prohibition, due to availability of non-synthetic alternatives, concerns about worker safety, effect on soil microorganisms, and possible contaminants. One reviewer supports allowance with restrictions on formulated products, but did not provide any support for validity of these measurements, which were found to be without basis by a research chemist.

Summary of TAP Reviewer's Analyses¹

<i>Synthetic/ Nonsynthetic</i>	<i>Allow without restrictions?</i>	<i>Allow only with restrictions? (See Reviewers' comments for restrictions)</i>
Synthetic (3) Nonsynthetic (0)	Yes (0) No (3)	Yes (1) No (2)

Identification

Chemical Names: Calcium oxide, CaO

CAS Number: 1305-78-8

Other Names:

Lime, burnt lime, burned lime, quicklime, calcium monoxide; pebble lime; unslaked lime; fluxing lime; Calcia.

Other Codes:

RTECS EW3100000
ICSC 0409
DOT-UN 1910
EPA PC Code: 075604

Characterization

Composition: 99.9% CaO, Ca 71.47%, O 28.53% . Properly stored commercial lime is 90-95% free CaO (Budavari, 1986). The molecular weight is 56.0794.

Properties:

It is white or gray, odorless lumps or powder, the melting point is 2572 °C, the boiling point is 2850 °C, and it readily absorbs oxygen and water from the air. It is soluble in water, forming calcium hydroxide and generating heat. Contact with water or moisture may generate enough heat to ignite nearby combustible materials. Calcium oxide is a strong caustic (Budavari, 1986; Hardy, 2001; NJDH, 1996).

How Made:

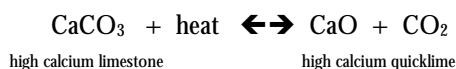
Calcium oxide is produced by burning (calcining) various forms of calcium carbonate such as limestone, marble, chalk, oyster shells, and dolomite. Lime burning was one of the first industries in the American colonies, in kilns dug out of the sides of hills. Stone age kilns used for burning lime have been discovered, and lime plaster in good condition is found on

¹ This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act to the best of the investigator's ability, and has been reviewed by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA [7 USC 6517(m)]. The information and advice presented to the NOSB is based on the technical evaluation against that criteria, and does not incorporate commercial availability, socio-economic impact, or other factors that the NOSB and the USDA may want to consider in making decisions.

Egyptian pyramids that are 4500 years old. The Greeks, Romans, Etruscans, Arabians, and Moors used lime plaster and mortar extensively in construction (Kirk-Othmer, 1991b).

The term “lime” is technically used only for burned forms of limestone such as quicklime or hydrated lime. However, the term is often broadly used to refer to limestone, which is primarily composed of calcium carbonate, but also may contain various amounts of magnesium carbonate. Other impurities are silica, iron, and aluminum. Limestone is classified by origin, chemical composition, texture, and geographical formation. Different sources of limestone used to produce quicklime result in different grades of purity of the calcium oxide product.

Limestone is quarried (usually in open pits), crushed, and screened. Dust control is a major environmental problem, requiring management from point sources and suppression at multiple points. The stone is then heated in kilns; typically a coal-fired rotary type in the US. The stone must be heated to the dissociation temperature of the carbonates, which is maintained for a certain duration while the carbon dioxide evolved must be rapidly removed. The reversible reaction is:



It takes approximately two tons of stone to produce one ton of quicklime, due to impurities and loss from dust. Energy requirements are high, from 5.5- 8 million Btus per short ton, depending on age and capacity of the kiln (Kirk-Othmer, 1991b).

Specific Uses:

More than 90% of the lime (burned or hydrated) produced in the United States is used for basic or industrial chemistry. The primary use is for steel manufacture (30%), metallurgy, air pollution control and water and sewage wastewater treatment (24%), cement and mortar, chemical manufacture, manufacture of glass and paper, diluents and carriers of pesticides such as lime-sulfur and Bordeaux mixture, and bleach production and other chemical manufacture (Kirk-Othmer 1991a, b; Budavari, 1986). Beet sugar refineries typically operate on-site lime kilns to provide both calcium oxide and carbon dioxide for the refining process, while cane sugar refining uses quicklime at a lesser rate (Kirk-Othmer, 1991b).

Calcium oxide or calcium hydroxide is used as liming materials for agricultural use, particularly when a rapid change in pH is desired. Calcium oxide may be difficult to use directly, as it immediately absorbs water after soil application, causing it to form flakes or granules that may harden due to re-formation of calcium carbonate. Caking can only be prevented by very thorough mixing when applied (Tisdale, 1985). Calcium oxide is pound for pound the most effective of commonly used liming materials, with a neutralizing value (calcium carbonate equivalent-CCE) of 179% for the pure material. Pure calcitic limestone has a rating of 100%, however most agricultural limestone rate the CCE as 90-95% because of impurities (Tisdale, 1985). More than 90% of the agricultural lime used in the US is calcium carbonate, next is magnesium-calcium carbonates (dolomitic limestone), and a much smaller percentage is calcium oxide or hydroxide (Miller, 1990). This is due to higher cost, lack of stability, caustic nature, and difficulty in handling (Miller, 1990; Parnes, 1990; Troeh, 1993; Brady, 1975; Zimmer, 2000). Burned lime may be used instead of limestone in order to minimize weight (Troeh, 1993).

Action:

In water, calcium oxide ionizes readily to form Ca^{++} and OH^- , forming a medium strong base or alkali. This effectively neutralizes acid soil solutions, and the calcium cation replaces aluminum on the cation exchange complex. In humid climates, such as the eastern US, most soils are acid due to leaching of soils and gradual depletion of bases in the soil cation exchange complex (Troeh, 1993; Engelstad, 1985). A neutral soil pH is desirable for most crops in order to tie up aluminum and iron, which can be toxic to plants at low pH. Other nutrients such as phosphorous and trace elements are more available at neutral pH (Parnes, 1990). Bacterial conversion of ammonium nitrogen to plant available nitrate forms is also stimulated by increased amounts of exchangeable base cations (Brady, 1975). Biological activity is also improved at neutral pH (Parnes, 1990; Brady, 1974; Pankhurst, 1997). Calcium is also an important plant nutrient, aside from its role in pH modification. Calcium is needed in cell membranes and growing shoots and root tips.

Combinations:

Calcium oxide (quicklime) used for agricultural applications is rarely in pure form; more commonly it is found in various combinations depending on the source of the parent material. Other minerals that may be present include magnesium (MgO), silica (SiO_2), iron (Fe_2O_3), and aluminum (AlO_3). “Air-slaked lime” contains a mixture of the oxide, hydroxide and carbonate of calcium or calcium and magnesium, derived from the exposure of quicklime (AAPFCO, 2000). Limestone parent materials may also include clay, in the form of alumina-silicates (Kirk-Othmer, 1991b). Kiln dust is a by-product of cement or burnt lime manufacture and contains calcium oxide and calcium hydroxide as well as some potassium and sulfur (Zimmer, 2000).

Slags are a group of industrial by-product materials and are used for their liming properties. Blast furnace slag is a by-product of pig iron, produced by reduction of iron by calcium carbonate, which produces calcium oxide. This calcium oxide combines the molten silica impurities from the iron to form a calcium silicate (CaSiO_3) that is cooled and ground. Another type of slag is known as basic or Thomas slag, and is the product of open hearth steel making from high phosphorus iron ores. Lime (calcium oxide) is used to flux the impurities of silica and phosphorous, and is usually applied for phosphorus content as well as liming qualities. Electric furnace slag is produced when phosphate rock is reduced to produce elemental phosphorous, and calcium oxide and silica fuse to produce a calcium silicate (Tisdale, 1985). Fly ash from coal burning power plants is produced when crushed coal and finely ground limestone are suspended and burned, so that the sulfur in the coal reacts to form gypsum (CaSO_4). The ash residue is a granular mixture of calcium oxide, calcium sulfate, and small amounts of metal oxides. Other industrial by-products that contain calcium oxide include flue dust from cement manufacturing, pulp mill lime, carbide lime, and by-products from the tanning industry (Tisdale, 1985; AAPFCO, 2000).

Status

Historic Use by Organic Farmers:

Neither calcium oxide nor the related form of calcium hydroxide is generally allowed for fertilizer use in organic farming. The NOSB refined the definition of synthetic in 1995 to declare that, "Heating and combustion of plants, animals, and microorganisms shall not be considered synthetic unless expressly prohibited in the National List. The combustion of minerals shall be considered synthetic and reviewed for compatibility under OFPA Sec 2119(m)(1-7)" (NOSB, 1995c). At the meeting in April 1995, the NOSB approved use of calcium hydroxide as a component of Bordeaux mix and lime sulfur, for fungicide use only (NOSB, 1995a). In November of 1995, NOSB approved use of hydrated lime for livestock with a suggested annotation that: "not permitted for soil application or to cauterize mutilations or deodorize animal wastes" (NOSB, 1995b).

OFPA, USDA Final Rule:

OFPA states in Sec. 6508(b):

"Soil Amendments. For a farm to be certified under this chapter, producers on such farm shall not

- 1) use any fertilizers containing synthetic ingredients or any commercially blended fertilizers containing materials prohibited under this chapter or under the applicable State organic certification program; or
- 2) use as a source of nitrogen, phosphorus, lime, or potash or any materials that are inconsistent with the applicable organic certification program."

Calcium oxide is not specifically listed anywhere in the NOP final rule. The NOP rule allows hydrated lime at 205.601(i)(3) and lime sulfur at 205.601(i)(5) for plant disease control. Lime sulfur is also listed as an insecticide at 205.601(e)(4). The NOSB voted in October 2001 that synthetic sources of calcium chloride (non-brine sources) are prohibited for crop use, and that nonsynthetic sources from the brine process may be used only as a foliar spray to treat physiological disorders related to calcium uptake. Calcium hydroxide is listed as an approved synthetic nonagricultural substance allowed as an ingredient in organic processed food at 205.605(b)(6).

Calcium oxide is approved by FDA at 21CFR 582.5210 as a substance Generally Recognized as Safe, and permitted for livestock feed, thus it appears to qualify for organic use as a feed additive under 205.603(d)(1), which allows "Trace minerals, used for enrichment or fortification when FDA approved." Technically speaking, calcium is not usually considered a trace mineral but a macro-mineral (Cheeke, 1999).

Regulatory: EPA/NIEHS/Other Sources

EPA: Office of Pesticide Programs Output reporting shows that of the four formerly active registrations, all uses have been cancelled, including tree wash and several forms of pulverized or pebble quick lime (EPA, 2002).

OSHA: legal airborne permissible exposure limit (PEL) is 5 mg/m³ over an 8-hour workshift.

NIOSH: airborne exposure limit is 2mg/m³ over 10 hour workshift.

ACGIH: American Conf. of Governmental Industrial Hygienists: threshold limit value 2mg/m³.

NFPA (National Fire Protection Association) rates as hazardous chemical: health – 1, slightly hazardous, breathing apparatus recommended, non-flammable, reactivity – 1: normally stable but may react with water.

NTP, IARC: not listed as a known carcinogen.

(Sources: MSDS- Mallinckrodt Baker, 1998; NJDH, 1996; Richardson 1993)

Status Among U.S. Certifiers

US certifiers prohibit the use of calcium oxide and calcium hydroxide as fertilizer. This includes OCIA, Farm Verified Organic, Oregon Tilth, MOSA, CCOF, NOFA chapters, MOFGA, QAI, WSDA, TDA (Texas Dept of Ag.), and New Mexico Organic Commodity Commission.

International

IFOAM Basic Standards 2000 – prohibited since not explicitly listed as approved.

EU 2092/91 – Prohibited, as Annex IIA does not list calcium oxide or calcium hydroxide, though it does list basic slag, and “Industrial Lime from sugar production.”

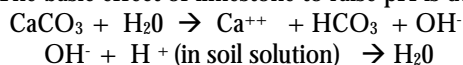
Canadian General Standards 1999 CGSB-32.310-99 – prohibited since not listed

Japanese Agricultural Standards – lists “Calcined lime” to be limited for use in Bordeaux mixture as fungicide.

CODEX – not listed. Does permit basic slag.

Section 2119 OFPA U.S.C. 6518(m)(1-7) Criteria**1. *The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.***

Liming materials are generally considered benign or beneficial when used to improve the soil pH for agronomic use. The basic effect of limestone to raise pH is due to the reactions:



The rate of this reaction depends on the amount of hydrogen ions (acidity) of the soil.

When limestone of medium fineness is added to soil, it results in calcium and magnesium being available in three forms: 1) as solid calcium or magnesium carbonates, 2) as exchangeable bases (Ca^{++}) that are adsorbed onto the soil colloids, or 3) as dissociated cations in the soil solution, mostly in association with bicarbonate ions (Brady, 1974). Use of an oxidized material such as calcium oxide produces a more rapid pH change, as it breaks down directly into calcium ion and the hydroxyl anion. This will favor a more rapid effect on the calcium ions in solution and adsorbed on the soil colloids. Both of these forms are subject to leaching. The reverse reaction is also possible: calcium oxide will readily hydrate in solution to form calcium hydroxide, which reacts with carbon dioxide in the soil to form calcium carbonate and bicarbonate. So, although calcium oxide will affect a rapid pH change, it is not stable and depending on soil conditions may eventually revert to insoluble forms (Brady, 1974; Parnes, 1990). Early studies comparing rates of reaction for different liming materials concluded that while hydrated lime reacted more quickly than high calcium limestone, differences largely disappeared after two months (Metzger, 1933).

Detrimental effects may occur due to difficulties in mixing, resulting in uneven concentrations, and the possibility of overliming. Excess lime can tie up available nutrients such as manganese, copper, zinc, and phosphorous. It also ties up boron. Rapid pH changes can also affect plants and microorganisms negatively when they cannot adjust quickly. For this reason, a well-buffered soil is considered more desirable (Brady, 1974). Overliming is possible where diverse soil conditions exist within a field, and in sandy conditions that may be deficient in micronutrients that will be further reduced in availability at high pH (Troeh, 1993).

2. *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.*

Sub-acute toxicity data: for rats: at repeated exposure inhalation at 413 mg/m³ or single exposure of 1026 mg/m³ found no deaths, no marked change in behavior or food intake (Richardson, 1993). It is not classed as a carcinogen by NIEHS/NTP.

It is reactive in soil, as it rapidly hydrolyses to calcium hydroxide, solubilizes into ionic form, or re-carbonates into calcium carbonate (Tisdale 1985; Brady, 1974). Some potential exists for leaching; this is similar to natural leaching of calcium from the soil complex.

Both calcium carbonate and calcium hydroxide applications to freshwater lakes suffering from eutrophication resulted in reduction of total phosphorus and macrophyte biomass resulting in improved water quality (Prepas, 2001). Treatments of ponds and canals with relatively high levels of slaked lime (210 mg/l for 65 hours) eliminated aquatic plants a month later. This result could not be reproduced in laboratory studies, and researchers theorized that the decline in biomass was due to short-term rise in pH in warm water, which resulted in low concentrations of free CO₂ and bicarbonate for biosynthesis (Chambers, 2001).

3. *The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.*

Calcium oxide is produced by heating mined calcium carbonate, requiring a large amount of energy. Dust is the major problem that must be closely monitored at various stages of mining and processing (Kirk-Othmer, 1991). Combinations found in by-product sources such as flue ash may be contaminated with iron, copper, lead, or other heavy metals (Stout, 1988; Pichtel and Hayes cited in Pankhurst, 1997).

4. *The effects of the substance on human health.*

Calcium oxide can severely irritate and burn the eyes and skin. Breathing the dust can irritate the lungs, causing coughing and shortness of breath. Higher exposures can cause fluid build-up in lungs and severe shortness of breath. Long-term exposure can irritate the nose, causing a hole in the inner nose, brittle nails, and cracking of the skin (NJDH, 1996). If ingested, it causes a burning sensation, abdominal pain, vomiting, and diarrhea (NIOSH, 1993). Contact with skin or mouth can cause thermal and caustic burns; eye contact causes dangerous clumps in the conjunctival sac (Gosselin, 1984). It can also cause severe irritation to eyes, blurred vision, ulceration, and loss of vision. Fatal burns and deaths from asphyxia have been reported after massive exposure (Richardson, 1993).

5. *The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock.*

Soil pH has a significant effect on the range and composition of soil organisms. Early researchers noted that low pH was injurious to some bacteria, especially the nitrifying bacteria, but favorable to development of fungi (Waksman, 1952). Addition of lime in the form of calcium carbonate was found to stimulate the increase in soil bacteria and increased decomposition of organic matter. Waksman noted that excess calcium carbonate could become injurious to soil bacteria, although no empirical studies were cited.

Earthworm populations are affected by pH, and are mostly absent from soils with extreme pH - over 8 or under 4 (Pankhurst, 1997). The addition of fertilizers such as ammonium salts was found to result in absence of earthworms, but specific comparison of liming materials was not reviewed. Different species of earthworms were found to favor different pH ranges between 5-8. The use of fertilizers is one of many agricultural practices that may have a large impact on population fluctuations of earthworms (Fraser 1994, cited in Pankhurst, 1997).

Use of fly ash as a liming material was found to have a negative impact on dehydrogenase enzyme activity, indicating suppression of overall microbial population. This was attributed to heavy metal contaminants in this material (Pichtel and Hayes, cited in Pankhurst, 1997). Changes in soil pH cause a rapid effect on protozoan populations, which respond positively to lime applications. Nematode populations also increase with liming (Pankhurst, 1997).

The TAP Review document prepared for NOSB in 1995 for hydrated lime states, "In direct soil application, however it would create a strong imbalance of soluble calcium which would negatively affect soil microbes and cause rapid oxidation of other soil nutrients" (NOSB, 1995d). While extensive reviews in Pankhurst did not directly consider effect of calcium oxide on microbes, extreme pH levels were found to generally reduce population levels. Other texts note the generally beneficial impact of lime on earthworms and microbes when pH is adjusted to optimal levels (Brady, 1974; Tisdale, 1985). An early study on the impact of limestone applied at different mesh sizes compared to hydrated lime in regards to nitrification rate found that both forms stimulated nitrification, with hydrated forms giving greater results (Walker, 1935).

The petitioner submitted data from experimental work with a proprietary complex containing calcium oxide and calcium hydroxide in combination with other materials to show that this complex did not negatively impact microbial degradation of cotton test strips as compared to a control, limestone application, or burnt lime treatment. Results were highly variable depending on site. Only one of three test sites showed a reduction in degradation rate due to application of burnt lime.

6. *The alternatives to using the substance in terms of practices or other available materials.*

The petitioner requested use of this material not as liming material but as calcium source for crop nutrition (Preston, 2001). Usually calcium deficiencies are associated with low pH soils and soils with a low cation exchanges capacity, such as a leached sandy soil. A standard remedy is to add limestone and build up soil organic matter (Magdoff, 2000). Mined sources can and do provide adequate available calcium to soils and plants in organic farming systems. The principle sources used by organic farmers are limestone, gypsum, and rock (tricalcium) phosphate. Rotations and compost can serve to increase the availability of these amendments. Wood ash and poultry manure also have readily available calcium (Parnes, 1990).

Gypsum (calcium sulfate) is widely used to supply calcium at neutral or higher pH (Tisdale, 1985; Troeh, 1995; Parnes, 1990; Brady, 1974). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been used as a fertilizer since early Greek and Roman times. Deposits are found at several locations in the US and Canada, and elsewhere in the world (Tisdale, 1985). Gypsum is widely used on saline-sodic soils to replace sodium on the soil colloids with calcium. The sulfur in the gypsum then precipitates with sodium and can be leached out of the soil. Gypsum is not a liming agent and has little effect on soil pH, but also provides sulfur, a necessary plant nutrient (Tisdale, 1985).

In non-organic systems, calcium fertilizers such as superphosphate and triple superphosphate contain 12-18% calcium. Calcium chelated materials may also be applied as foliar sprays.

Normally the large amount of exchangeable calcium on the colloidal complex satisfies the calcium needs of most crops (Mortvedt and Cox in Engelstad, 1985; Troeh, 1995). Some crops have shown calcium deficiency when soil acidity is not a problem; these are usually localized in fruits, storage organs, or shoot tips. Examples include poor kernel formation in peanuts, bitter pit in apples, blossom end rot in tomatoes, tipburn in lettuce, and black heart of celery (Mortvedt, in Engelstad, 1985). Gypsum applications are effective at supplementing calcium in peanuts (Tisdale, 1985). Foliar applications of calcium chloride are effective when translocation of calcium is a problem to actively growing shoots and fruits (see 2001 TAP review of calcium chloride).

Calcium ions on the soil exchange surfaces are not very mobile, and the plants take up calcium ions more readily from the soil solution (Troeh, 1993). Calcium in solution is in dynamic equilibrium with the exchangeable form, so that when calcium is removed by plants or by leaching, there is replacement by the adsorbed phase (Tisdale, 1985). If there is a sudden addition to calcium in solution, then more adsorption on to the exchange complex can also be expected. Factors determining calcium supply to plants include a number of factors, including total calcium supply, soil pH, CEC, percent calcium saturation of soil colloids, type of soil colloids, and the ratio of calcium to other cations in solution (Tisdale, 1985). A study comparing the effectiveness of different liming materials found that the order of effectiveness in neutralizing acidity was hydrated lime, basic slag, cement kiln dust, and ground limestone. All of these different materials showed increasing response in plant uptake of calcium when applied at increasing rates, based on calcium equivalency, but there was no difference between lime sources (Oguntoyinbo, 1996). Another study comparing liming materials found that efficiency increased with decreased Mg content and that silicates were less effective than carbonates or oxides. Efficiency of carbonate forms increases with fineness of grinding (Gutser, 1987).

Limestone fineness directly affects the rate of solubility of calcium cations (Brady, 1974; Miller, 1990). Where a rapid pH change is desired, use of a more finely ground limestone will effect a quicker change. Limestone can be evaluated for effective calcium carbonate equivalent (ECCE) or effective neutralizing value (ENV) based on a formula derived from the fineness and chemical nature of the liming material (Troeh, 1993). If at least 50% of a limestone will pass through a 100 mesh screen, it is considered fine limestone, and gives good results. Theoretically, if 100% of a ground stone passed through a 100 mesh screen, a pH change would be complete within 3 months (Miller, 1990). Limestone that passes a 60% screen should be completely reacted in soil within three years. Fluid limestone formulations are also available, consisting of finely ground limestone suspended in water with clay (Miller, 1990).

Fertilizer sources of calcium (Parnes, 1990)

	<u>Ca content lbs./ton</u>	<u>lime equivalent, lbs./ton</u>
poultry manures	80	
legume hay	28	
clam and oyster shells	680	1700
wood ashes	700	1750
rock phosphate	420-660	800-1200
calcitic limestone	760	1900
dolomitic limestone	500	1900
gypsum	460	

7. *Its compatibility with a system of sustainable agriculture.*

The Principles of Organic Production and Handling adopted by the NOSB include as goals the “use [of] cultural, biological, and mechanical methods, as opposed to using synthetic materials to fulfill specific functions within the system” and describes an organic systems production system as one designed to:

“Optimize soil biological activity; Maintain long-term fertility;...Recycle materials of plant and animal origin in order to return nutrients to the land, thus minimizing the use of non-renewable resources, (and) Minimize pollution of soil, water, and air” (NOSB, 2001).

The use of nonsynthetic liming materials such as limestone (a nonrenewable resource) is unavoidable in humid climates where soil naturally becomes acid and base cations leach out over time. Increased attention to organic matter additions and use of renewable resources such as poultry manures and wood ashes may be practical in some systems but not all. Use of synthetic calcium oxide contributes indirectly to increased energy use and fossil fuel consumption due to the burning process of manufacture. Natural sources of mined limestone or gypsum are more slowly soluble and contribute to soil fertility and neutralization over a longer term. Some sources of mixed calcium oxides and silicates are usable recycled materials from industrial pollution control systems, iron production, or cement kilns, but these may also contain metal and other contaminants. A neutral pH is beneficial to the soil organisms, but rapid pH changes may cause short term fluctuations and disruptions in population levels.

TAP Reviewer Discussion

Reviewer 1 [Ph.D. plant pathology, M.S. soil science. Research, consulting, and administrative activities related to waste treatment and reuse of waste as soil amendments and fertilizers. Southeast US]

Comments on Database

The following information needs to be corrected or added to the database:

Under the Combinations section, the review mentions that kiln dust is a by-product of cement or burnt lime manufacture. In addition to the calcium oxide and calcium hydroxide mentioned in cement kiln dust, there are a variety of other chemicals. Some cement kilns are permitted to burn hazardous waste as a fuel source. The MSDS for cement kiln dust lists a variety of heavy metals that it may contain including lead antimony, arsenic, mercury, and others. The route of exposure for many of these metal is through inhalation or ingestion (Ash Grove Cement Co., 2000).

OFPA Criteria Evaluation

(1) The potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;

The criteria evaluation needs to be corrected or amended as follows:

The petitioner information suggests using calcium oxide as a source of calcium as a plant nutrient. Gypsum is a better source of calcium as a plant nutrient than calcium oxide. Gypsum satisfied the calcium needs of peanuts better than lime and does not modify soil pH (Kamprath and Foy, 1985; Parnes, 1990). Many soils have large amounts of calcium on the exchange complex that are sufficient to supply most crops calcium needs (Kamprath and Foy, 1985).

(2) The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;

I agree with the criteria evaluation.

(3) the probability of environmental contamination during manufacture, use, misuse or disposal of such substance;

Other combination materials may include lime kiln dust, which contains calcium oxide, magnesium oxide, calcium, carbonate, and silica (Peters Chemical Co.). There is increasing interest in the agricultural use of industrial combustion by-products such as fly ash that have a high pH (Pankhurst, 1997). Cement kilns often own limerock mines because limerock is the primary feedstock of cement kilns. Lime kiln dust may come from cement kilns that are permitted to burn hazardous waste, which can be used as a fuel source source (Peters Chemical Co., website; Hansen, 1990).

In 1999, the US EPA proposed management of cement kiln dust under the Resource Conservation and Recovery ACT (RCRA). The US EPA included proposed limitations on various pollutants in cement kiln dust that would be used for agricultural purposes (US EPA, 1999; US EPA, 1998). Cement kilns are also significant point sources for air pollution. Pollutants include carbon monoxide, sulfur dioxide, nitrogen oxides, and particulates.

(4) the effect of the substance on human health;

I agree with the criteria evaluation.

(5) the effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;

The use of nitrogen fertilizers results in an increase in soil acidity, which creates the need for more frequent lime applications (Kamprath and Foy, 1985; Troeh and Thompson, 1993). Waksman (1952) found that calcium carbonate stimulated soil bacteria, which led to an increased decomposition of soil organic matter. The humus fraction of soil organic matter provides long term benefits including pH buffering, increased cation exchange capacity which is pH dependent, and water holding capacity (Bohn et al., 1979; Haynes and Naidu, 1998).

Although this petition is for calcium oxide, the petitioner also submitted information pertaining to a proprietary product called Bio-Cal. Included in this information was research that examined the effects of Bio-Cal, calcium oxide, and calcium carbonate on soil biological activity. Buried cotton strips were used as a bioassay to measure microbial activity. This is an indirect method to assay microbial activity. It was not accompanied by soil assays for target decomposing organisms but rather for broad classes of microorganisms. The results of this field research were statistically quite variable and did not correlate with the Formazan bioassay results for microbial activity. The authors also mention a previous study that showed increased microbial activity with Bio-Cal rather than no difference. At this point in time their results are too variable to draw conclusions about the impacts of different lime materials on microbial activity.

(6) the alternatives to using the substance in terms of practices or other available materials; and
[reviewer corrections incorporated above]

(7) *its compatibility with a system of sustainable agriculture.*

I agree with the criteria evaluation.

Reviewer 1 Conclusion – *Summarize why it should be allowed or prohibited for use in organic systems.*

Calcium oxide is a synthetic material due to its production via the combustion of limestone.

Lime to correct calcium deficiency is rarely needed. If calcium is needed, an option is gypsum, which will provide calcium without significantly affecting the soil pH (Tisdale et al., 1985). Poultry manure and legume green manures are also sources of calcium. Lime is predominately used to correct soil pH. The use of inorganic nitrogen fertilizers has increased the need for lime through their acidifying affect (Kamprath and Foy, 1985; Troeh and Thompson, 1993). Current organic standards allow the use of calcium carbonate and dolomite to correct soil pH.

Calcium oxide is also extremely caustic material to handle and causes damage to the respiratory tract. Products used in organic agriculture should strive to reduce risks to farm worker health.

Finally, calcium oxide is also a component of cement kiln dust, which is a by-product of the cement kiln industry (MSDS Ash Grove Cement Co.). Many cement kilns burn hazardous waste and tires for fuel (Hansen, 1990 and 1992). The US EPA has proposed restrictions on various pollutants in cement kiln dust that will be used for agricultural purposes (US EPA, 1998).

Reviewer 1 Recommendation Advised to the NOSB:

The substance is Synthetic

For Crops, the substance should be Not Added to the National List.

Reviewer 2 [Ph.D. Research chemist, serves on an organic certification committee, Eastern US]

Comments on Database

I find the database (Characterization and Status) to be reasonably complete and fairly accurate.

OFPA Criteria Evaluation

I agree with the criteria evaluation in the database, and offer additional supporting information.

(1) the potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;

CaO is extremely caustic. Its reaction with water or organic acids (urine) releases a large amount of heat. Addition of water directly to CaO (accidental or otherwise) can generate temperatures as high as 800° C. (NFPA, 78). Ignition of straw and powdered sulfur caused by water/CaO reaction have been reported. Fire fighters are advised to avoid using water on CaO during a fire unless the danger from other burning material is greater than the risks associated with the CaO/water reaction (NFPA, 1978).

The pH of a saturated solution of CaO is about 12.5, which is much higher than that of CaCO₃ (9.4) (Weast, 81). It is easy to overlime with CaO, which would tie up plant nutrients like Boron (Parnes, 90), and harm soil biota (see below).

(2) the toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;

Solid CaO is an irritant causing chemical burns and inflammation of plant or animal tissue (Gosselin et al., 1976). Aqueous CaO [Ca(OH)₂] harms organisms primarily through high pH. A study of the use of Ca(OH)₂ as a disinfectant against *Cryptosporidium parvum* oocysts in water supplies found that calcium hydroxide only killed oocyst through high pH (Robertson et al., 1992). The hydroxide has no effect on *C. parvum* when the pH is adjusted down to 6. In the Eastern US, Ca(OH)₂ will not persist in the soil. Reaction with atmospheric CO₂ and acidic rain water will destroy any hydroxide. This conversion takes some time, however, and local high pH conditions can persist around the lime particles.

(3) the probability of environmental contamination during manufacture, use, misuse or disposal of such substance;

The main environmental problem is dust generated by the kiln firing and powder processing (milling & screening, and packaging). Workers at these plants are advised to wear protective clothing to avoid skin and eye exposure and use a respirator (not single use or quarter-mask respirator) (NIOSH, 1994).

(4) the effect of the substance on human health;

Irritation of skin and eyes, and inflammation of mucus membranes and lungs are the main immediate health effects of CaO exposure. The NIOSH 10 hour time-weighted average human exposure is 2 mg/cu meter and the immediate health danger limit is 25 mg/cu m. (NIOSH, 1994).

(5) the effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;

Little literature exists on the effect of CaO and Ca(OH)₂ on soil organisms. The aqueous hydroxide of calcium is used as an antimicrobial and there exists an extensive literature on its effect on microbe pathogens. (OH)⁻ ions are antimicrobial at pH > 9 and will inhibit most bacteria and many viruses (Aiello, 1998). CaO soaked in water [Ca(OH)₂] is also used to disinfect premises (Aiello, 1998).

In human dentistry, Ca(OH)₂ is used as an antibacterial agent in root canals (intracanal dressing) and in periodontal work (Estrela et al., 2001; Molander et al., 1999). Stuart et al., 1991, found Ca(OH)₂ to be effective in vitro against *Streptococcus mutans*, *Actinomyces viscosus* and *Bacteroides gingivalis*.

Scarification of seeds to enhance germination can favor colonization by pathogenic bacteria. Holliday et al., 2001, found reduction in *Salmonella* and *Escherichia coli* O157:H7 when alfalfa seeds (for sprouts) were treated in 1 % Ca(OH)₂. The presence of organic material in the seed did not affect the antimicrobial activity.

Field studies of the effect of liming on soil fauna are difficult to control. Raising soil pH > 6 favors fungi and worm populations over bacteria (Waksmen, 1952; Dick, 1997). pH shifts also alter the availability of nutrients. Nitrogen mineralization can be effected by both pH and changes in the bacteria/fungi populations. Weyman-Kaczmarkowa and Pedziwilk (2000) studied the effect of liming on soil microbes in sandy loam and loose sand soil. They used Ca(OH)₂ to increase the soil pH and found that the total microbial biomass (bacteria + fungi) decreased by ~ 50 % when pH was raised from the natural 4.5 to 9.0 in the sandy soil. In the loam (natural pH of 7.7) using Ca(OH)₂ to raise the pH to 9.0 decreased the biomass by 30 %, and an increase to pH = 11 decreased biomass by 40%.

A study of different liming materials on soil microbial activity is attached to the petition. This study uses buried cotton strips to measure microbial activity in soils limed with limestone, burnt lime and a brand named product Bio-Cal. Biologic activity is measured by the amount of the strips that decomposed during the 1999 growing season. The study is difficult to interpret. The liming products are not described in enough detail to allow one to assess their relative liming abilities (particle size, CEC). An earlier study in 1998 by the same group used limestone milled much finer than typical field grade lime (Zimmer, 1999). This limestone would have higher Ca availability than field grade limestone and its effect on soil would be more similar to that of the other liming materials tested.

In the 1999 study, four replicates were run for each material in each field. The data scatters badly for all amendments at two sites. At a third site (a garden soil), the scatter drops and the author attempts a Student's t-test of the population means. The results reported show that some of the liming materials can be differentiated at the 2% significance level. A Student t-test to determine if two overlapping populations are distinct assumes that the two populations follow a normal distribution. If limited data suggest that they do have normal distribution, a minimum of five data points for each are usually needed (BBN, 1988). If there is no indication that they are gaussian, then a sample size of 50 is usually indicated. Analysis of the four data points for each liming material using probability and box plots shows no indication that the data are normally distributed. Some of the data visually appear to be outliers, but there are too few data for the box plot routine to flag them as such.

(6) the alternatives to using the substance in terms of practices or other available materials

As stated above, all the basic Ca lime materials affect soil pH and Ca availability the same way. The higher the acid neutralizing power and the calcium solubility are, the faster the effects will be seen in the field. Limestone and gypsum are slower acting than the synthetic calcium oxides but do the same job. Quality pastures with high nutrient grasses are possible using mined limestone and gypsum. Three to five years may be needed to optimize pastures using the mined minerals, however (Nation, 1995). The synthetics work faster, but possible can do harm to soil biota.

(7) its compatibility with a system of sustainable agriculture

Mined liming and Ca field amendments are compatible with sustainable agriculture. The main US limestone deposits are found in the Mid-West, but mineable deposits are found through out the Appalachian and Rocky Mountains (Brobst & Pratt, 1973). CaO is usually produced at limestone quarries. It is synthesized at high temperatures (1000° C.) in open kilns that require large inputs of energy (Vorres, 1991). Since the un-fired limestone is an adequate liming material, the additional processing and energy use seems unnecessary.

A discussion of the petitioned annotation for CaO.

The petition requests that CaO be placed on the National List only if it is in a form that yields less than one degree F [increase in temperature] when mixed with 1:1 vol. water. This request is based on crude calimetry data provided by an analytical testing lab. The lab measured a heat of solution for the product Bio-Cal of 0.6 cal./gm. Assuming that all the material was CaO, the measured heat of solution would be 0.14 kJ/mole, far lower that the traditional CaO value of 63.6

kJ/mole (Kirk-Othmer, 1991b). No controls of known chemistry are reported to validate the test method. 0.6 cal/gm is a much lower heat of solution than any of the Ca liming materials used to make the product.

The heat of solution of a chemical compound is a thermodynamic state function. It is as diagnostic of a specific chemical as the chemical composition or the X-ray diffraction pattern. If CaO were added to the National List of Allowed Synthetics with the annotation “only if it is in a form that yield less than one degree F increase in temperature when mixed with 1:1 vol. water”, one would be essentially saying that CaO would be an allowed synthetic only if it does not behave like CaO. If a thermo state property does not define a chemical, then what property does define that compound? How can one prove that a substance on a product’s list of ingredients is the synthetic that is on the National List?

Much of the documents attached to the petition pertain to a brand name product, Bio-Cal. Bio-Cal is a processed liming material, which uses feed stocks of kiln dust ($\text{CaO} + \text{Ca(OH)}_2$), gypsum, and power plant fly ash. Fly ash varies in chemical composition, but is basically a Mg, Fe alkaline earth aluminosilicate (Bone & Himus, 1936). These feed stocks are mixed/milled and heated by a proprietary process to give a final product, which has apparent low heat of solution and high Ca availability (see petition). The pH of 17 lots of Bio-Cal average 12.3 (± 0.4), which is slightly lower than Ca(OH)_2 . Neither the chemical composition of Bio-Cal nor the processing temperature are given. The final product is probably more than just a mixture of Ca(OH)_2 , CaCO_3 and CaSO_4 . These phases may exist with reaction rims and precipitated particles of complex hydroxy carbonates and hydroxy sulphates like $\text{Ca}_2(\text{H}_2\text{O})[\text{SO}_3]_2$ (Bassanite) or $\text{Ca}(\text{H}_2\text{O})_6[\text{CO}_3]$ (hexahydrocalcite) (Povarennykh, 1972).

Reviewer 2 Conclusion

CaO is used as an antimicrobial in the medical and food industries. Limited field data suggest that it is harmful to soil biota. All the benefits of CaO additions to soil can be obtained by the addition of mined limestone and gypsum.

Calcium oxide is a crystalline solid. Its crystal structure is Isometric with space group Fm3m. It is generally unstable when moisture is present and exhibits a large exothermic reaction with water to form aqueous Ca(OH)_2 . The heat of solution in water for CaO is 64 kJ/mole. CaO has a distinct from its precursor CaCO_3 , which possesses a different chemical composition, crystal structure (Trigonal with space group R3_c), and heat of solution in water (13.1 kJ/mole).

Commercial CaO is synthetic. Natural CaO can form during high temperature contact metamorphism in rock invaded by igneous magma (Berry & Mason 59). It is rare, however, and not commercially exploitable.

CaO is synthetically produced by heating limestone or dolomite in a kiln. Production usually occurs in limestone quarries to minimize transportation costs. CaO is not stable in moist air and will convert to solid Ca(OH)_2 . Calcium hydroxide has more industrial uses than CaO and most limestone that is fired to lime is further processed to the hydroxide.

The three basic Ca compounds derived from limestone-- CaCO_3 , Ca(OH)_2 , and CaO--are all used as agricultural field amendments. Limestone can be simply crushed to a desired particle size, while the other two compounds are only used for ag purposes if their powder size or purity are not acceptable for higher value applications.

These basic calcium compounds serve two main purposes as and field amendments. The anion raises the pH of acidic soils. The ability of these compounds to raise pH is determined on the amount of acid each molecule can neutralize (CaO has the highest neutralizing value, Tisdale et al., 1985). The particle size of the liming agent is also important in pH control. Coarse particles have lower surface area than fine ones and take longer to react with soil water and acids. Milling CaCO_3 very fine can speed the kinetics of the neutralization and make the limestone behave more like CaO. A mole of CaCO_3 , however, neutralizes less acid than CaO (Norton & Zhang, 1998), and more limestone would be needed to achieve the final pH of a given amount of CaO. Many ag crops grow best in neutral pH soils. Neutral to slightly basic soil pH binds toxic ions like Al and Fe while releasing other ions needed for plant growth and health (Zimmer, 2000).

Calcium released by solution of the carbonate or hydroxide also competes with Na^+ and Al^{+3} ions for absorption sites on clay particles. Increasing exchangeable Ca^{+2} loosens soil structure and facilitates plant uptake of other minerals (Norton & Zhang, 1998; Tisdale et al., 1985). Gypsum (CaSO_4) behaves like calcium compounds in its effect on soil texture and plant mineral uptake. The sulfate anion, however, does not change soil pH and does not effect mineral availability in the soil like lime does.

Effective use of gypsum and basic calcium liming materials can have very positive effects on the yield and nutrition of crops and grass forages (Nation, 1995; Zimmer, 2000). Any of the three basic calcium compounds can be used to achieve these effects. The amount of Ca applied and the neutralizing capacity is different for the three compounds, but can be tuned by varying the amount of each compound applied to the soil. The kinetics can also be partially controlled by the choice of particle size used.

Calcium oxide is a synthetic compound. It should be prohibited without annotation for use as a field amendment.

Calcium oxide, which has an unusually low heat of solution, cannot be reviewed due to a lack of consistent properties.

Reviewer 2: Recommendation Advised to the NOSB

The substance is Synthetic

For Crops and Livestock, the substance should be Not Added to the National List.

Reviewer #3 [Organic farmer, organic inspector, advises organic certifier. Western US.]

Comments on Database

Materials provided with the TAP Review appeared to be consistent and helpful in understanding what the detrimental and positive effects of calcium oxide can be.

This material should be considered synthetic. It is currently allowed for use for disease control as a foliar but is prohibited as a fertilizer. The concern over its use as a fertilizer is that it creates a strong imbalance of soluble calcium, which negatively affects soil microbes and causes rapid oxidation of other soil nutrients.

Producers certified by some chapters of OCIA and OGBA have used these materials in formulations [that meet the proposed restrictions] for many years. In this sense, the materials have previously been accepted for use in organic agriculture....

OEPA Criteria Evaluation

Alternatives:

There are many existing alternatives for adjusting pH that are currently used in organic agriculture. This particular form and formulation has several significant advantages and mitigates some of the disadvantages.

The approved organic alternatives work well but do not have some of the beneficial properties of this formulation. A distinction needs to be made between the formulation, Bio-Cal, and the generic ingredients, calcium oxide and calcium hydroxide. The Bio-Cal contains several ingredients of which calcium oxide and calcium hydroxide are a part.

The effects of the formulation is different from the effects of each separate ingredient. The request is to allow the generic material to be used in a manner that has effects similar to a proprietary formulation. According to some data [provided by the petitioner] this formulation is several times more efficient at providing calcium to plants and soil than either the approved organic alternatives or the petitioned [generic] materials.

Is the material compatible with organic production and handling?

With the restrictions requested in the application--specifically the requirements that it be applied in a form that yields less than 1degree Fahrenheit temperature increase when equal volumes of product and water are mixed and that it be part of a managed program to remineralize soils--the negative effects on the soil are mitigated. The material with restrictions is compatible with organic agriculture.

Recent developments and insights into the "soilfoodweb" have developed organic agriculture practices and enhanced our understanding of what developing soil means in terms of microorganisms. Formulations or amendments that increase the activity and number of species of soil microorganisms should be considered compatible with organic agriculture. The restriction that this material be applied to the fields in amounts necessary to raise soil minerals to optimum levels based on soil tests is also likely to increase diversity of microorganisms.

The same material without restrictions has been found to have detrimental effects to the soil. In common terms, it "burns the soil and kills the worms." Some data suggests the effects may not be as harmful for the first applications, instead the harmful effects build up over time and in conjunction with other practices.

The material is synthetic and alternative materials are available to adjust pH and protect plants from disease.

Other considerations

This petition brings up a larger issue with some important implications for considering what materials should be allowed for use in organic agriculture. The larger issue is: if a material that can cause harm when used conventionally can be restricted or reformulated in a manner that does not cause harm, should it be allowed? If it is allowed, what quantitative measurement of harm should it be judged by?

The measurement of harm should be based on our increasing understanding of soil and plant microbiology. What it means to "build the soil" can now be defined by measurement of the diversity of microorganisms. Soil building is fundamental to

the principals of organic agriculture and specified in the Final Rule in 205.203 (a) "The producer must select and implement tillage and cultivation practices that maintain and improve.... biological condition of soil...." Soil building is a method of increasing fertility, pest and disease control for crop production.

If a material is either neutral or increases the diversity of microorganisms, it should be considered beneficial to the soil. A material that enhances the diversity of microorganisms can be considered safe for the environment, producer, field workers, and consumer and therefore allowed for use in organic agriculture.... The significance of using soil microbial components and soil enzyme activities as indicators for monitoring the impact of materials on soil is gaining recognition. It is also very significant to organic agriculture....

In the case of calcium oxide, one of the main harmful effects of the material is the heating (oxidation) of the soil. An evaluation method that measures the amount of heat a given formulation produces is a valid evaluation method. The restriction that limits the amount of heat produced is appropriate for organic agriculture. Unfortunately, there does not appear to be protocols established as to how to measure this effect. The manufacturer's test has the advantage of being simple to perform at the farm level.

In the petition there were several documented questionnaires from organic growers testifying to their support for Bio-Cal. *[In this reviewers opinion]* long term support for a material from organic growers is significant factor in considering a material's organic status.

The material has long been recommended for use as disease control in "Bordeaux mixture." This mixture is effective for its toxicity and is not usually considered part of a soil building regime or beneficial to microorganisms. It does however show the material has been accepted for other aspects of organic crop production

Reviewer 3 Conclusion

I recommend that it be approved as synthetic-allowed with requested restrictions on its use. *[The proposed]* restrictions protect the soil from excessive oxidation ("burning") that can be caused by using too high a concentration. It also prohibits direct application of the material in raw form. To meet this restriction, the material must be formulated with other materials before being applied to the soil. It can be used as an ingredient, but not directly.

The restriction *[also]* limits the amount of material that can be applied and requires soil testing..*[and]* requires further documentation on its use and limits the amount of material used.

Reviewer 3: Recommendation Advised to the NOSB

The substance is Synthetic.

For Crops and Livestock, the substance should be Added to the National List with restrictions.

Suggested Annotation: It is applied in a form that yields less than 1 degree Fahrenheit temperature increase when equal volumes of product and water are mixed. It is applied to fields in amounts necessary to raise soil minerals to optimum levels based on soil tests. It is applied as part of a managed program to remineralize soils.

[End of TAP Reviewer Comments]

TAP Conclusion:

All three reviewers find calcium oxide to be a synthetic material. Two of the reviewers support prohibition, and find that there are nonsynthetic alternatives, as well as concerns about worker safety, possible effects on microorganisms, and possibility of contaminants. One reviewer supports allowance with restrictions on formulated products proposed by the petitioner, however did not offer any validation or support for this method of determining heat of solution. A research chemist reviewer noted that, "No controls of known chemistry are reported to validate the test method." Calcium carbonate (limestone), gypsum, the use of legume cover crops, and poultry manure are nonsynthetic alternatives widely used in organic soil building programs.

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